



CASE PP/15-22821/A/CGM 520/PCT

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

IN RE PCT NATIONAL STAGE APPLICATION OF  
HENDRIK WERMTER ET AL  
INTERNATIONAL APPLICATION NO.  
**PCT/EP 04/000068**

Group Art Unit: **1796**

Examiner: **Katarzyna I. Wyrozebski Lee**

**Confirmation No. 8680**

FILED: **January 8, 2004**

FOR: STABILIZATION OF THERMOPLASTIC  
NANOCOMPOSITES

U.S. APPLICATION NO: **10/542,045**

35 USC 371 DATE: July 13, 2005

Commissioner for Patents  
P.O. Box 1450  
Alexandria, VA 22313-1450

**DECLARATION UNDER RULE 132**

I, Rainer Xalter, a citizen of the Federal Republic of Germany, residing in 67063 Ludwigshafen, Germany, hereby declare:

**CREDENTIALS**

1. That I was awarded the degree of a Doctor of Natural Sciences by the Albert-Ludwigs-University of Freiburg, Germany in 2008.

2. That I have been employed by Ciba Spezialitätenchemie GmbH as research chemist since October 2007 and presently hold the position of Head of Project Laboratory / Polymer Design in the Plastic Additives Segment.

3. That I am the author or co-author of the following publications in the field of nano-composites:  
R. Xalter, T. S. Halbach, R. Mülhaupt: New polyolefin nanocomposites and catalyst supports based on organophilic boehmites, *Macromolecular Symposia* **2006**, 236, 145-150.

R. Xalter, F. Pelascini, R. Mülhaupt: Ethylene polymerization, on-line particle growth monitoring, and in situ nanocomposite formation using catalysts supported on arylsulfonic acid-modified boehmites, *Macromolecules* **2008**, 41, 3136-3143.

4. I submit herewith results from comparative tests that were carried out under my guidance and supervision:

## COMPARATIVE PROCEDURES

### General Description

#### **Compounding**

84.95 parts Moplen HF 500 N (polypropylene, Basell Polyolefins, Germany), 15.00 parts Polybond 3200 (maleic anhydride grafted polypropylene, Chemtura, U.S.), and 0.05 parts calcium stearate are pre-mixed in a laboratory mixer. For the preparation of the compounds, 500 g of this mixture are mixed with the appropriate amounts of filler and additives as listed in Tables 1-3 and extruded in a twin-screw extruder (ZSK 25, Coperion Werner&Pfleiderer, Germany) at 230 °C and a screw speed of 100 rpm.

#### **OIT Measurements**

Thin slices of 15±2 mg were cut from the extruded strands. Measurements of the OIT (oxidation induction time) of these samples are performed according to ASTM D 3895-80 and DIN EN 728, respectively, at 200°C and an oxygen flow of 50 mL/min using a thermogravimetric analyzer (TG 209 F1, Netzsch). The calculated DTA (differential thermal analysis) curve is used for the determination of the OIT. A higher OIT value is indicative of a better stabilization of the respective sample.

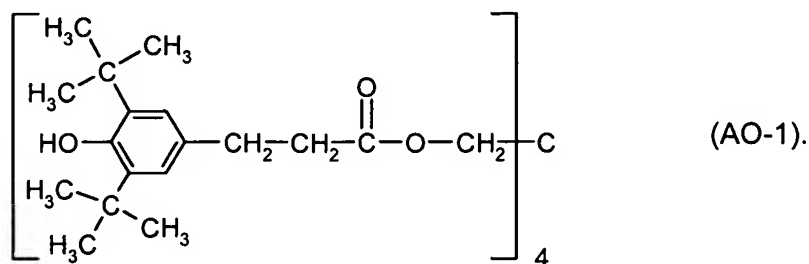
## Materials

Araldite GT 7072 bis-phenol A type from Huntsman Inc; 1.68-1.75 Epoxy Equivalents/kg

Irganox B 225 is a 1:1 mixture of Irganox 1010 and Irgaphos 168 from Ciba Inc.

Irgafos 168 (RTM) (Ciba Specialty Chemicals Inc.) is tris(2,4-di-tert-butylphenyl) phosphite.

Irganox 1010 (RTM) (Ciba Specialty Chemicals Inc.) is a compound of the formula AO-1



Cloisite Na<sup>+</sup> (RTM) is a natural montmorillonite from Rockwood Inc.

Cloisite 20A (RTM) is a modified monmorillonite in nano-scaled form

## Results

**Table 1: Comparative examples: Unmodified filler (microfiller) at 5% loading**

Example	B225 [%]	Cloisite Na <sup>+</sup> [%]	Araldite GT 7072 [%]	OIT [min]
1-1	0.3			9.9
1-2	0.3	5		32.5
1-3	0.3	5	0.6	15.4

**Table 2: Comparative examples: Unmodified filler (microfiller) at 20% loading**

Example	B225 [%]	Cloisite Na <sup>+</sup> [%]	Araldite GT 7072 [%]	OIT [min]
2-1	0.3			9.9
2-2	0.3	20		2.7
2-3	0.3	20	0.6	7.0

**Table 3: Inventive examples: Organically modified filler (nanoclay) at 5% loading**

Example	B225 [%]	Cloisite 20A [%]	Araldite GT 7072 [%]	OIT [min]
3-1	0.3			9.9
3-2	0.3	5		7.5
3-3	0.3	5	0.6	13.0

Explanations to the comparative examples.

3 series of experiments have been carried out which are presented in Tables 1-3.

Table 1 shows the results of classically filled polymers with a low degree of filler (5 wt.-%), which would be typical for nano scaled fillers. Stabilization with Irganox B 225 (phenolic antioxidant and phosphite process stabilizer) alone results in an OIT of 9.9 minutes. The addition of 5 wt.-% Cloisite Na<sup>+</sup> results in an improvement up to 32.5 minutes. Further addition of Araldit GT 7072 (bisphenol A type epoxide) significantly decreases the value down to 15.4 minutes.

In other words, in a classically filled polymer with low degree of filling the addition of the epoxide is detrimental.

Table 2 shows the results of classically filled polymers with a conventional degree of filler (20 wt.-%, see Fumitoshi). Stabilization with Irganox B 225 (phenolic antioxidant and phosphite process stabilizer) alone results again in an OIT of 9.9 minutes. The addition of 20 wt.-% Cloisite Na<sup>+</sup> results in reduction down to 2.7 minutes. Further addition of Araldit GT 7072 (bisphenol A type epoxide) improves the OIT value up to 7.0 minutes, the value of the unfilled system, however, is not reached.

In other words, in a classically filled polymer with conventional degree of filling the addition of the epoxide improves the OIT value. However, the stability of the unfilled sample is not reached.

Table 3, Example 3.3 shows the result which is obtained according to the instant invention. Stabilization with Irganox B 225 (phenolic antioxidant and phosphite process stabilizer) alone results, in an OIT of 9.9 minutes. Addition of 5 wt.-% Cloisite 20A (nano-scaled phyllosilicate) reduces the OIT value to 7.5 minutes (compare Table 1 classically filled system with 5 wt.-% degree of filling where an improvement has been observed). Further addition of Araldit GT 7072 (bisphenol A type epoxide) improves the OIT value significantly up to 13.0 minutes which is definitely higher than the OIT value of the unfilled sample.

## CONCLUSIONS

5. These results clearly demonstrate the superior performance of the instant additive composition in polymers which are filled with nano-scaled phyllosilicates as compared to conventionally filled prior art polymers.

This is surprising, since there is no teaching in the prior art which would have motivated the artisan to use such additive compositions with the expectation of an improved over all performance.

## FINAL STATEMENT

I, Rainer Xalter, declare further that all statements made herein of personal knowledge are true and all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

Signed this            day of            , 2009.

Rainer Xalter